Magnetic and Electric Phase Control in Epitaxial $EuTiO_3$ from First Principles

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(Dated: February 4, 2008)

We propose a design strategy - based on the coupling of spins, optical phonons, and strain - for systems in which magnetic (electric) phase control can be achieved by an applied electric (magnetic) field. Using first-principles density-functional theory calculations, we present a realization of this strategy for the magnetic perovskite $EuTiO_3$.

There is great interest in multiferroic materials in which ferroelectric (FE) and ferromagnetic (FM) ordering not only coexist, but in which the electrical polarization **P** and the magnetization **M** are large and strongly coupled [1, 2]. One challenge in identifying strongly coupled FM-FE's that has received considerable attention in the past [3] is the scarcity of such materials in nature, as most insulators (a requirement for ferroelectricity) are paraelectric (PE) and antiferromagnetic (AFM). With the recent advances in first-principles density-functional methods for predicting [4] and in novel synthetic techniques for growing new FM-FE multiferroics, the focus has now turned to how to produce a strong coupling between the two distinct order parameters [5]. Recently, attention has focused on a mechanism in which magnetic order itself breaks inversion symmetry [6, 7, 8, 9]. Based on this, remarkable control of the FE state by an applied magnetic field has been demonstrated in some rare-earth manganites [10, 11], however, the natural scale of the spontaneous polarization thus induced is very small, of the order of nC/cm^2. Furthermore, the magnetic state appears to be rather insensitive to an applied electric field for this class of materials.

As a result, it is clearly advantageous to explore other possible mechanisms for strongly coupled multiferroism. A fruitful starting point for identifying such mechanisms is the observation, recently discussed by Tokura [5], that the basic physics of a strong **M-P** coupling involves a competition between different ordered states, e.g. between a FM-FE state and an AFM-PE state. In this Letter, we present a new approach for designing a strongly coupled multiferroic in which the interplay of spins, optical phonons, and strain leads to such a competition.

The criteria that a system must satisfy for this proposed mechanism to be realized are as follows: (1) It must be an AFM-PE insulator in which at least one infrared-active (ir) phonon is coupled to the magnetic order, (2) the spins in the AFM ground state should align with the application of a magnetic field of modest strength, (3) this alignment should decrease the frequency of the spin-coupled ir-active phonon, and, (4) the key to our approach, the ir-active mode of interest must be strongly coupled to strain. Epitaxial strain can have profound effects on the properties of thin films [12]. In our design strategy we use epitaxial strain to dial into the region of the phase diagram where a spin-phonon-driven destabilization of the lattice actually occurs. The FM-FE phase thus produced is a low-lying state competing with the AFM-PE ground state. As a direct result of this competition, magnetic and electric phase control can be achieved by an applied electric and magnetic field respectively. As the polarization of the low-lying FM-FE phase results from the freezing-in of a soft polar phonon triggered by the spin-phonon coupling, it is of the same order of magnitude as prototypical soft-mode FEs ($\mu C/cm^2$). In addition, as the phase-control region is approached from the low strain side, the magnetocapacitance diverges, while on the high strain side there may be, in some cases, a phase boundary between the AFM-PE phase control region and a true equilibrium FM-FE phase. The use of epitaxial strain to exploit the relatively modest spin-phonon effects displayed by many bulk materials provides an exciting new design strategy in the pursuit of strong **M-P** coupled multiferroics.

In bulk, europium titanate $EuTiO_3$ is an AFM-PE that crystallizes in the cubic perovskite structure (space group $Pm\bar{3}m$) with room temperature lattice constant equal to that of $SrTiO_3$, a=3.905Å. The Eu^{2+} moments (J=S=7/2) order at T_N=5.5K [13, 14, 15] while neutron diffraction studies indicate G-type AFM order [15]. Both diffraction and local structural probes [16] (XANES) support $EuTiO_3$ remaining cubic at all temperatures. Recently, Katsufuji and Takagi [13] (KT) showed that at the onset of AFM order, the static dielectric constant ϵ_0 undergoes a sharp reduction of about 10%, indicating a hardening of the lattice. Further, KT demonstrated that in an increasing magnetic field ϵ_0 increases, saturating at a field large enough to fully align the spins (approximately 1.5 T). KT argue and, as we will see, our first-principles calculations confirm, this behavior is due to a coupling between the spins and an ir-active phonon of the type $\omega = \omega_{PM} + \lambda\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ [17, 18]. These bulk measurements show that $EuTiO_3$ satisfies the first three criteria, and a close structural analogy to $SrTiO_3$ suggests that it satisfies the key fourth criterion. In the remainder of the Letter we present a first-principles calculation of the ground-state epitaxial phase diagram for $EuTiO_3$ demonstrating that this system is indeed a realization of our proposed mechanism for strongly coupled multiferroicity.

Within density-functional theory, the failure of the generalized gradient approximation (GGA) properly to capture the physics of strongly correlated systems is well established. A widely accepted approach beyond GGA is the GGA plus Hubbard U (GGA+U) method [19]. We perform first-principles density-functional calculations using projector augmented-wave potentials within spin-polarized GGA+U approximation as implemented in the *Vienna ab initio Simulation Package* [20, 21] with a plane wave cutoff of 500 eV and a 6×6×6 Γ-centered k-point mesh. The PAW potential for Eu treated the $4f^7$ $5s^3$ $5p^6$ $6s^2$ as valence states. All calculations were performed with collinear spins and without LS-coupling. As expected for Eu^{2+} which lacks orbital degrees of freedom, inclusion of LS-coupling does not change the results. Values of the Eu on-site Coulomb, U = 6 eV, and exchange, J_H=1.0 eV, parameters were used that give a reasonable account of the magnetic exchange constants which were extracted by mapping GGA+U calculations of the total energy for different spin configurations at T=0 onto a classical Heisenberg model; $E_{spin}=-\sum_{ij} J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$ (note, in our notation the energy per spin bond is $2J$). Phonon frequencies and eigendisplacements were calculated using the direct method where each ion was moved by approximately 0.01Å. Born effective charge tensors were calculated by finite differences of the polarization using the modern theory of polarization [22] as implemented in VASP. Before we proceed we note that calculations with GGA+U overestimate lattice constant a by ∼1%. Therfore, we introduce a shift of the zero for σ_{33}, the out-of-plane component of the stress, so that σ_{33}=0 for the cubic structure at the experimental lattice constant, a_{exp}= 3.9Å. Thus, the correct cubic structure is obtained at misfit strain $\eta\equiv(a_{exp}-a)/a_{exp}$=0.

First, to examine the validity of a spin-phonon coupling mechanism in bulk $EuTiO_3$ we performed first-principles density-functional calculations of the ir-active phonons and the Born effective charges, allowing us to evaluate ϵ_0 of a single-domain, stoichiometric, defect-free crystal. To elucidate the role of magnetic order on the phonons and subsequently the dielectric response, we calculate the quantities just mentioned with the Eu spins in two different magnetic configurations: FM and G-type AFM. All calculations for cubic $EuTiO_3$ were carried out at the experimental lattice constant a_0 = 3.90 Å. The calculated magnetic exchange constants were found to be in good agreement with experiment (shown in parentheses): J_1 = -0.013 K (-0.014 K), J_2 = +0.065 K (+0.037 K); the positive sign for J_2 is consistent with the unusual positive sign of the Curie-Weiss temperature for AFM $EuTiO_3$. The ground state is thus correctly found to be G-type AFM, with the FM state higher in energy by 0.2 meV per formula unit. For the static dielectric constant, we find ϵ_0 = 350 for $EuTiO_3$ with FM order and ϵ_0 = 280 with AFM order. These values compare well with the experimental values of 420 and 380 in fields of 1.5 T and 0 T, respectively [13]. The spin-dependence of the dielectric response is due entirely to the lowest-lying ir-active phonon TO1, which we calculate to be at 70 cm^{-1} and 77 cm^{-1} for FM and AFM respectively. This good agreement of the relative magnitudes of the values for ϵ_0 with the size of the experimentally measured field-induced change confirms KT's suggestion that the magnetocapacitive effect in bulk $EuTiO_3$ is indeed due to spin-phonon coupling, with the sign of the coupling λ such that FM spin alignment reduces the stability of the low-frequency polar phonon.

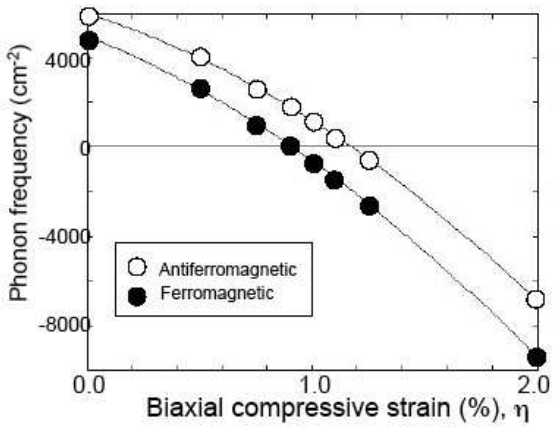

FIG. 1: Soft ir-active phonon frequency squared, ω^2, (cm^{-2}) of paraelectric $EuTiO_3$ as a function of compressive epitaxial strain η. Space group for $\eta\neq0$ is P4/mmm; the phonon is polarized along the tetragonal axis, with symmetry label A_{2u}.

Next, we consider the effects of epitaxial strain. In perovskite titanates such as $SrTiO_3$ and $BaTiO_3$, it is well known both experimentally and theoretically that epitaxial strain couples strongly to the low lying TO1 polar mode. For example, in $SrTiO_3$, a modest epitaxial strain of less than 1% transforms the PE bulk material into a room-temperature FE [23], with **P** of nearly 20 μC cm^{-2} [24]. As the calculated eigendisplacement pattern of this polar mode for $EuTiO_3$ is virtually identical to that of the soft polar mode previously calculated for $SrTiO_3$ and $BaTiO_3$, it is natural to expect similar strain coupling, with the spin-phonon coupling in $EuTiO_3$ adding richness to the phase diagram.

We isolate the effects of epitaxial strain, as in previous phenomenological and first-principles studies [25, 26, 27], by imposing the epitaxial constraint on the lattice parameters of the infinite crystal with periodic boundary conditions, corresponding to zero macroscopic electric field. For simplicity, in the present study we consider only compressive strain. We focus attention on the lowest-lying ir-active phonon TO1 which as mentioned above dominates the spin-dependent dielectric response in cubic $EuTiO_3$ and any possible FE instability. In the cubic phase, TO1 is 3-fold degenerate, where each phonon mode is polar-

ized along one of the three Cartesian coordinates. Under a biaxial compressive strain in the a-b plane, the lattice expands along the c-axis, conserving volume to a first approximation. This lowers the symmetry of $EuTiO_3$ from cubic to tetragonal, splitting the 3-fold degenerate TO1 mode into a two-fold E_u and one-fold A_{2u} degenerate mode polarized perpendicular and parallel to the c-axis respectively. Under compressive strain, the E_u modes harden and are not relevant to our study.

In Fig. 1, we show the evolution of the lowest-lying ir-active A_{2u} phonon frequency with biaxial compressive strain η for FM and AFM $EuTiO_3$. At η=0, we have bulk $EuTiO_3$ where $\omega_{A_{2u}}=\omega_{TO1}$ = 70 cm^{-1} and 77 cm^{-1} for FM and AFM respectively, as we previously discussed. With increasing compressive strain, the A_{2u} phonon frequency decreases for both types of magnetic order. At approximately η_{c1}=0.92%, the FM system develops a polar instability as evidenced by the vanishing ir-active phonon frequency. On the other hand, the AFM system remains stable up to approximately η_{c2}=1.2%. Thus, in the intermediate strain regime between $\eta\approx$0.92% and $\eta\approx$1.2%, $EuTiO_3$ has a low-lying FM-FE state in competition with a AFM-PE state, exactly the conditions which have been identified as facilitating strong **M**-**P** coupling.

It is this difference in the FE instability for the AFM and FM orderings that leads to a giant magnetocapacitive effect near the critical strains, η_c. To see this, in Fig. 2(a) we show the component of the static dielectric tensor along the c-axis, ϵ_{33}, calculated from first principles [28] for both AFM and FM ordering. In each case, as the frequency of the polar mode goes to zero at the corresponding η_c, the dielectric response diverges. For example, at η=0.9%, we find $\epsilon_{33}\approx 10^3$ for the ground state AFM-PE phase. If a magnetic field is applied that aligns the spins into FM ordering, ϵ_{33} increases 50-fold to that of the FM-PE phase, $\epsilon_{33}\approx 5\times10^4$. Since the AFM-PE response remains finite as η_{c1} is approached while the FM-PE response diverges, the magnetocapacitance diverges in the vicinity of the phase boundary.

Once the critical strain is crossed for each ordering, the unstable polar phonon freezes in and the ground state crystallographic symmetry becomes $P4mm$. In Fig. 2(b), we show the computed spontaneous polarization for the relaxed ground state structures as a function of epitaxial strain. A large **P**-η coupling is evident for both orderings. For strains above 1.2%, the AFM state also become FE, but the range of strains over which the AFM-FE state is the ground state is extremely narrow, with a first-order transition to the FM-FE phase occurring at $\eta \approx$ 1.25%. At this phase boundary, the polarization in the FM phase is already over 10 μC cm^{-2}. Thus, we show that a previous unknown multiferroic phase of $EuTiO_3$, with a symmetry-allowed linear magnetoelectric effect, can be stabilized by readily accessible epitaxial strains.

The most interesting behavior in this system is produced in the intermediate strain region, $\eta_{c1} < \eta < \eta_{c2}$, under applied electric $\mathcal{E}$ or magnetic $\mathcal{H}$ fields. We obtain a qualitative understanding of the phase diagram to leading order by adding the terms $-\mathbf{M}\cdot\mathcal{H}$ and $-\mathbf{P}\cdot\mathcal{E}$ to the energy, and taking **M** and **P** to have their zero-field values. For example, at η=1.0% the ground state is still the AFM-PE phase but the application of a magnetic field of sufficient strength to fully align the spins, $\mathcal{O}$(1T) (the same order as that found by KT for the bulk), induces a substantial spontaneous polarization $\mathbf{P}\approx 10\mu$C cm^{-2}, by driving the system into the FM-FE phase. Notably, **P** is several orders of magnitude greater than the polarization of all previously known FEs whose origin is through a coupling to spins. In addition, at η=1.0% the application of an electric field, $\mathcal{O}(10^5$V cm$^{-1})$ (small for thin films) favors the polar FE phase over that of the non-polar PE phase, inducing a magnetization of $7\mu_b$ by driving the system into the FM-FE phase. We summarize the results for compressive strain in Fig. 3.

From these estimates, both magnetic control of the electric phase and electric control of the magnetic phase in epitaxially strained $EuTiO_3$ should be easily attain-

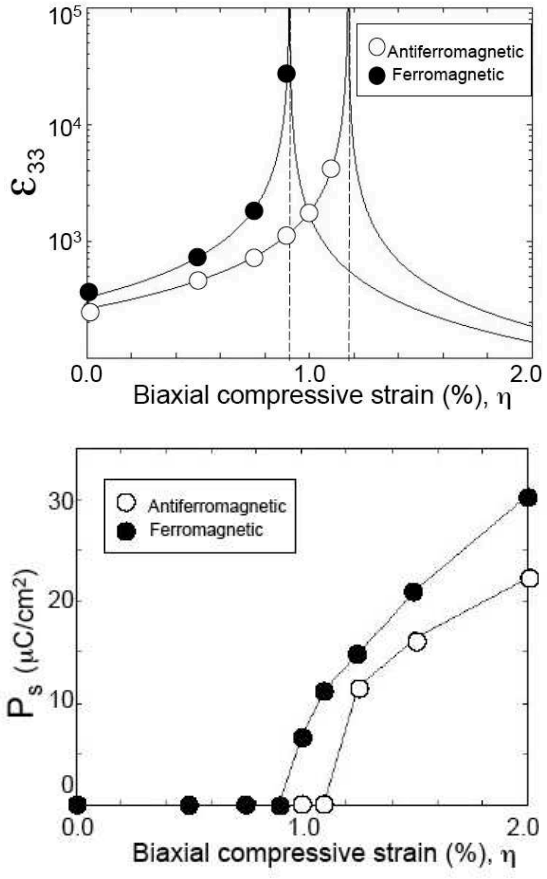

FIG. 2: (Top) Static dielectric constant ϵ_{33} and (bottom) spontaneous polarization P_s as a function of epitaxial compressive strain η. For ϵ_{33}, the solid lines are fits proportional to $(\eta$-$\eta_c)^{-1}$ while the dashed vertical lines indicate η_c.

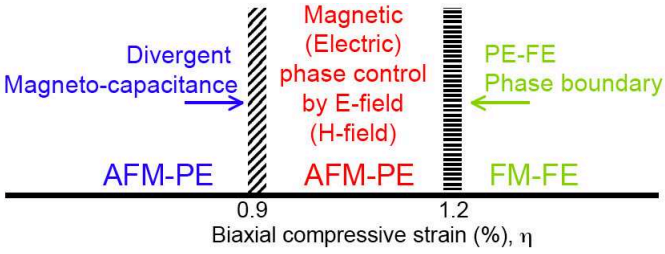

FIG. 3: $EuTiO_3$: Compressive epitaxial strain (η) phase diagram.

able experimentally. However, the symmetry of the PE-paramagnetic structure determines the lowest order spin-phonon coupling (the origin of the discussed effects) as a bi-quadratic effect $\mathcal{F}_{int} \propto \mathbf{M}^2\mathbf{P}^2$. So, while an applied magnetic field can turn the polarization on from zero, there is no preferred direction and the magnetic field does not act to reversibly switch the polarization between symmetry-related orientations. At present, such switching has only been demonstrated in multiferroics with minute polarizations [10, 11]. Similarly, an applied electric field cannot be used to reversibly switch between different magnetization states [29], though it can turn a substantial magnetization on from zero.

In further analogy to $SrTiO_3$, effects similar to those descibed above in $EuTiO_3$ are expected not only for compressive, but also for tensile epitaxial strain; first-principles investigations are in progress. The recent success in fabricating high-quality thin films of $EuTiO_3$ with zero epitaxial strain [30] is encouraging for experimental realization of the predicted effects. While we have focused on the example of $EuTiO_3$, we expect that additional materials with the necessary characteristics could be identified and their epitaxial phase diagrams explored.

In summary we have presented a realization of a new mechanism for strong coupling between magnetic and ferroelectric ordering. The required material characteristics are a spin-phonon coupling through which FM spin alignment softens a low-frequency polar mode that is strongly coupled to epitaxial strain. The predicted competition between an AFM-PE phase and a FM-FE phase allows magnetic phase control with an applied electric field, and electric phase control with an applied magnetic field, with modest critical fields. In addition to being a promising mechanism by which such phase-control can be achieved, we anticipate that epitaxial stabilization of a FM-FE ground state - such as that which occurs in $EuTiO_3$ above strains $\approx 1.25\%$ - over the bulk AFM-PE phase may also prove to be a useful avenue to the identification of new FM insulators suitable for spintronics applications.

We thank D. G. Schlom and D. Vanderbilt for useful discussions. This work was supported by NSF DMR-05-07146. CJF acknowledges support from Bell Labs and Rutgers University.

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